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Inorganic and Organozinc Fluorocarboxylates: Synthesis, Structure and Materials Chemistry

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Abstract

The organozinc fluoro-carboxylates $RZnO_2CR_f$ and $RZnO_2CR_f \cdot TMEDA$, along with $Zn(O_2CR_f)_2 \cdot TMEDA$ ($R = Me, Et$; $R_f = C_2F_5, C_3F_7$) have been synthesised. The structures of $EtZnO_2C_2F_5$ (**5**), $EtZnO_2C_3F_7$ (**7**), $EtZnO_2C_2F_5 \cdot TMEDA$ (**11**), $Zn(O_2C_2F_5)_2 \cdot TMEDA$ (**13**), along with products from the adventitious reaction with either O_2 or H_2O , $Zn_{10}Me_4(OMe)_4(O_2CC_2F_5)_{12}$ (**2**), $Zn_9Et_2(O_2CC_2F_5)_{12}(O)_2$ (**6**), $Zn_8Et_4(OEt)_4(O_2CC_3F_7)_6(O)$ (**8**), $[Zn(O_2CC_3F_7)_2 \cdot TMEDA]_2 \cdot H_2O$ (**15**) have been determined. Thin films of oriented ZnO have been deposited on glass substrates by low-pressure chemical vapour deposition (LPCVD) using **3** and **10** as precursors, though no fluorine incorporation in the films was noted. LPCVD using **13** as precursor also yielded fluorine-free ZnO, but lacking the oriented growth observed using **3**, **10**. However, **5**, which exhibits short intermolecular $Zn \dots F$ contacts in the solid state, thermally decomposes to bulk ZnF_2 .

Introduction

Zinc carboxylates have long attracted the interest of chemists due to their fundamental roles in biological systems,¹ as catalysts (for example, co-polymerisation of CO₂ / epoxides,²⁻³ cyclopropanation⁴ among others⁵), hydrogen storage⁶ and as secondary building units for a vast array of metal-organic frameworks (MOFs).⁷⁻⁹ As a result, in excess of 5000 zinc carboxylate structures can be found in the Cambridge Crystallographic database, though, remarkably, only 16 are organozinc carboxylates of which 12 adopt a conventional RZn(O₂CR') arrangement.

Our interest in this area is the possible use of volatile zinc carboxylates as precursors for ZnO materials. ZnO has a hexagonal wurtzite structure and is a wide bandgap semiconductor with a bandgap of 3.3eV;¹⁰ conductivity can be increased with the addition of dopants such as B,¹¹ Al,¹² Ga,¹³ In.¹⁴ In particular, we are interested in fluorine-doped zinc oxide (ZnO:F)¹⁵ as an alternative transparent conducting oxide (TCO) to the more common In₂O₃:Sn (ITO) or fluorine-doped tin oxide (FTO). In ZnO:F, fluorine atoms enter the ZnO lattice in substitutional form; Gordon *et. al* have theorised that due to this, fluorine doping gives the lowest resistivity to ZnO.¹⁵ ZnO:F has been identified as having the highest transparency and being one of the least toxic TCOs, as well as being cheap and abundant, both pre-requisites for sustainable commercial exploitation.¹⁶

Thin films of ZnO:F have been deposited using spray pyrolysis,¹⁷ sol-gel spin coating¹⁸ and sputtering.¹⁹ Gordon *et. al* have studied the deposition of ZnO:F by CVD extensively and have deposited films initially using a multi-source approach, i.e. Et₂Zn, EtOH and C₃F₆ and later using Et₂Zn.TMEDA, EtOH and C₆H₅C(O)F. The earlier precursors in particular grew high quality films with a very low sheet resistance of 5Ω/square and a visible absorption of 3%.^{10,15} We have previously used organotin fluorocarboxylates to successfully deposit FTO,²⁰ and have now attempted to use the same methodology for ZnO:F. While a search of the Cambridge Crystallographic database reveals numerous structures containing the Zn(O₂CCF₃) moiety, only two reports concern more fluorinated carboxylic acid derivatives of zinc.²¹⁻²²

Experimental

All operations were carried out under an atmosphere of dry dinitrogen or argon using standard Schlenk and glove-box techniques. Hexane, dichloromethane and tetrahydrofuran solvents were dried using an Innovative Technology, Inc. Solvent Purification System (SPS) system and degassed under dinitrogen or argon prior to use. Deuterated THF and chloroform (C₆D₆) NMR solvents were purchased from Aldrich and

dried over molecular sieves before use. All dry solvents were stored under dinitrogen or argon in Young's flasks over 4 Å molecular sieves.

^1H and ^{13}C NMR experiments were performed at ambient temperature using a Bruker Avance-300; ^1H and ^{13}C NMR chemical shifts are referenced internally to residual non-deuterated solvent resonances. ^{19}F NMR experiments were performed at ambient temperature using a Bruker Avance-400 and reference internally to residual non-deuterated solvent resonances. All chemical shifts are reported in δ (ppm) and coupling constants in Hz. The following abbreviations have been used for multiplicities: s (singlet), d (doublet), t (triplet), q (quartet), sept (septet), br (broad), m (unresolved multiplet). Elemental analyses were performed externally by Stephen Boyer of London Metropolitan University, UK using a Carlo Erba Flash 2000 Organic Elemental Analyzer. Thermogravimetric analyses (TGA) were performed using a Perkin Elmer TGA 4000 Thermogravimetric Analyzer,

Synthesis

*Synthesis of $[\text{MeZn}(\text{O}_2\text{CC}_2\text{F}_5)]_n$ (**1**):* $\text{C}_2\text{F}_5\text{COOH}$ (0.65 g, 4.0 mmol) was added to a stirred solution of Me_2Zn (2 ml of 2M solution in hexane, 4.0 mmol) in hexane (10 ml) at -78°C . Solution was stirred overnight while slowly warming up to room temperature, a white precipitate remained. Solution was warmed to 50°C , leaving a clear solution, crystals were obtained on slow cooling of the solution to room temperature (0.61 g, 63 %, mp $115\text{--}116^\circ\text{C}$). Analysis found (calc. for $\text{C}_4\text{H}_3\text{F}_5\text{O}_2\text{Zn}$): C 19.8 (19.8), H 1.2 (1.3) %. ^1H NMR (300 MHz, THF- d^8) δ ppm: -0.81 (s, 3H, CH_3), ^{13}C NMR (300 MHz, CDCl_3) δ ppm: 163.2 (br. s, CO_2), 119.8 (qt, $J = 286.6, 35.4$ Hz, CF_3), 108.0 (tq, $J = 264.2, 37.2$ Hz, CF_2), -18.2 (br. s, CH_3), ^{19}F NMR (400 MHz, THF- d^8) δ ppm: -85.7 (br. s, CF_3), -123.0 (br. s, CF_2)

*Synthesis of $\text{Zn}_{10}\text{Me}_4(\text{OMe})_4(\text{O}_2\text{CC}_2\text{F}_5)_{12}$ (**2**):* Initial attempts to recrystallize **1** with the addition of CH_2Cl_2 (10 ml) and cooling to 5°C produced **2** (0.38 g, 41 %, mp $81\text{--}83^\circ\text{C}$). Analysis found (calc. for $\text{C}_{22}\text{H}_{12}\text{F}_{30}\text{O}_{14}\text{Zn}_5$): C 19.3 (19.0), H 1.0 (0.9) %. ^1H NMR (300 MHz, THF- d^8) δ ppm: 3.44 (br. s, 3H, OCH_3), -0.81 (s, 3H, ZnCH_3), ^{13}C NMR (300 MHz, CDCl_3) δ ppm: 163.7 (br. s, CO_2), 119.8 (qt, $J = 285.9, 36.6$ Hz, CF_3), 108.0 (tq, $J = 262.4, 37.8$ Hz, CF_2), 53.8 (br. s, OCH_3), -18.2 (br. s, CH_3), ^{19}F NMR (400 MHz, THF- d^8) δ ppm: -83.8 (s, CF_3), -121.2 (s, CF_2)

Synthesis of [MeZn(O₂CC₃F₇)]_n (3): Prepared using the same synthesis method as **1** using C₂F₅COOH (0.86 g, 4.0 mmol) and Me₂Zn (2 ml of 2M solution in hexane, 4.0 mmol); yield 0.72 g, 62 %, mp 81-83 °C.

Analysis found (calc. for C₅H₃F₇O₂Zn): C 20.5 (20.6), H 1.2 (1.0) %. ¹H NMR (300 MHz, THF- *d*⁸) δ ppm: -0.80 (s, 3H, CH₃), ¹³C NMR (300 MHz, CDCl₃) δ ppm: 165.5 (br. s, CO₂), 119.0 (qt, *J* = 288.2, 34.3 Hz, CF₃), 109.8 (tsxt, *J* = 266.3, 34.3, CF₂CF₃), 109.6 (tt, *J* = 265.3, 33.30 Hz, O₂CCF₂), -18.4 (br. s, CH₃), ¹⁹F NMR (500 MHz, CDCl₃) δ ppm: -82.4 (br. s, CF₃), -119.1 (br. s, CF₂), -128.3 (br. s, CF₂)

Synthesis of Zn₁₀Me₄(OMe)₄(O₂CC₃F₇)₁₂ (4): Initial attempts to recrystallize **3** with the addition of CH₂Cl₂ (10 ml) and cooling to 5°C produced **4**; yield 0.41 g, 36 %, mp 141-142 °C. Analysis found (calc. for C₂₈H₁₂F₄₂O₁₄Zn₅): C 19.8 (19.9), H 0.8 (0.7) %. ¹H NMR (300 MHz, THF- *d*⁸) δ ppm: 3.52 (br. s, 3H, OCH₃), -0.84 (s, 3H, ZnCH₃) ¹³C NMR (300 MHz, CDCl₃) δ ppm: 162.5 (br. s, CO₂), 117.5 (qt, *J* = 286.6, 34.7 Hz, CF₃), 108.3 (tsxt, *J* = 266.1, 39.1 Hz, CF₂CF₃), 108.2 (tt, *J* = 267.3, 32.9 Hz, O₂CCF₂), 52.2 (br. s, OCH₃), -6.1 (s, ZnCH₃), ¹⁹F NMR (400 MHz, THF- *d*⁸) δ ppm: -81.8 (s, CF₃), -118.5 (br. s, CF₂), -127.9 (s, CF₂)

Synthesis of [EtZn(O₂CC₂F₅)]_n (5): Prepared using the same synthesis method as **1** using C₂F₅COOH (0.65 g, 4.0 mmol) and Et₂Zn (4 ml of 1M solution in hexane, 4.0 mmol), leaving a clear solution with a small amount of white precipitate. Crystals were obtained from was from filtering the solution and cooling to -20°C (0.71 g, 70 %, mp 89-91 °C). Analysis found (calc. for C₅H₅F₅O₂Zn): C 23.6 (23.4), H 1.9 (2.0) %. ¹H NMR (500 MHz, THF- *d*⁸) δ ppm: 1.17 (t, *J* = 8.04 Hz, 3H, CH₃), 0.21 (q, *J* = 8.20 Hz, 2H, CH₂), ¹³C NMR (500 MHz, THF- *d*⁸) δ ppm: 164.1 (br. s, CO₂), 119.7 (qt, *J* = 284.3, 34.5 Hz, CF₃), 108.0 (tq, *J* = 264.3, 37.2 Hz, CF₂), 12.6 (s, CH₃), -2.7 (br. s, CH₂), ¹⁹F NMR (500 MHz, THF- *d*⁸) δ ppm: -83.9 (br. s, CF₃), -121.2 (br. s, CF₂)

Synthesis of Zn₉Et₂(O₂CC₂F₅)₁₂(O)₂ (6): From synthesis of **5**, the small amount of white precipitate was dissolved in CH₂Cl₂ (10 ml) and hexane (10 ml), solution was filtered and colourless crystals were obtained on cooling to 5 °C (0.09 g, 10 %, mp 134-136 °C). Analysis found (calc. for C₄₀H₁₀F₆₀O₂₆Zn₉): C 18.2 (18.3), H 0.5 (0.4) %.

Synthesis of [EtZn(O₂CC₃F₇)]_n (7): Prepared using the same synthesis method as **1** using C₂F₅COOH (0.86 g, 4.0 mmol) and Et₂Zn (4 ml of 1M solution in hexane, 4.0 mmol); yield 0.79 g, 65 %, mp 96-99 °C. Analysis

found (calc. for $C_6H_5F_7O_2Zn$): C 22.6 (23.5), H 1.6 (1.7) %. 1H NMR (300 MHz, THF- d^8) δ ppm: 1.17 (t, J = 7.91 Hz, 3H, CH_3), 0.21 (q, J = 8.10 Hz, 2H, CH_2), ^{13}C NMR (500 MHz, $CDCl_3$) δ ppm: 162.9 (br. s, CO_2), 119.1 (qt, J = 288.0, 33.4 Hz, CF_3), 109.8 (tsxt, J = 264.2, 35.3 Hz, CF_2CF_3), 109.6 (tt, J = 264.2, 35.5 Hz, $CF_2CF_2CF_3$), 12.6 (s, CH_3), -2.8 (s, CH_2), ^{19}F NMR (500 MHz, $CDCl_3$) δ ppm: -81.8 (br. s, CF_3), -118.4 (br. s, CF_2), -127.8 (br. s, CF_2)

$Zn_8Et_4(OEt)_4(O_2CC_3F_7)_6(O)$ (**8**): Initial attempts to recrystallize **7** with the addition of CH_2Cl_2 (10 ml) and cooling to 5°C produced **8** (0.43 g, 41 %, mp 115-117 °C). Analysis found (calc. for $C_{40}H_{40}F_{42}O_{17}Zn_8$): C 22.7 (22.8), H 1.9 (1.9) %. 1H NMR (300 MHz, $CDCl_3$) δ ppm: 3.74 (q, J = 7.03 Hz, 2H, OCH_2), 1.07 (t, J = 7.20 Hz, 3H, OCH_2CH_3), 0.96 (t, J = 7.90 Hz, 3H, $ZnCH_2CH_3$), -0.01 (q, J = 7.91 Hz, 2 H, $ZnCH_2$), ^{13}C NMR (300 MHz, $CDCl_3$) δ ppm: 165.0 (br. s, CO_2), 119.1 (qt, J = 286.1, 36.2 Hz, CF_3), 109.9 (tsxt, J = 266.1, 36.2, Hz, CF_2CF_3), 109.8 (tt, J = 267.0, 34.3 Hz, $CF_2CF_2CF_3$), 63.7 (br. s., OCH_2), 21.3 (br. s., OCH_2CH_3), 12.7 (s, $ZnCH_2CH_3$), -2.51 (br. s., $ZnCH_2$), ^{19}F NMR (400 MHz, THF- d^8) δ ppm: -81.8 (s, CF_3), -118.5 (br. s, CF_2), -127.8 (s, CF_2)

*Synthesis of $MeZn(O_2CC_2F_5)TMEDA$ (**9**):* C_2F_5COOH (0.65 g, 4.0mmol) was added to a stirred solution of Me_2Zn (3 ml of 2M solution in hexane, 6.0 mmol) and $TMEDA$ (0.47g, 4.0 mmol) in hexane (10 ml) at -78 °C. Solution was stirred overnight while slowly warming up to room temperature. Solvent and volatiles were removed *in vacuo*, a colourless oil remained (0.94 g, 66 %, mp 119-120 °C). Analysis found (calc. for $C_{10}H_{19}F_5N_2O_2Zn$): C 33.4 (33.5), H 5.3 (5.4), N 7.7 (7.8) %. 1H NMR (300 MHz, THF- d^8) δ ppm: 2.68 (s, 4H, NCH_2), 2.44 (s, 12H, NCH_3), -0.93 (s, 3H, $ZnCH_3$), ^{13}C NMR (300 MHz, THF- d^8) δ ppm: 161.6 (t, J = 24.8 Hz, CO_2), 120.2 (qt, J = 285.9, 36.0 Hz, CF_3), 108.1 (tq, J = 260.5, 36.6 Hz, CF_2), 57.7 (s, NCH_2), 46.9 (s, NCH_3), -18.7 (s, $ZnCH_3$), ^{19}F NMR (400MHz, THF- d^8) δ ppm: -85.5 (CF_3), -122.7 (CF_2)

Also prepared by the same method:

*$MeZn(O_2CC_3F_7)TMEDA$ (**10**):* Using C_3F_7COOH (0.86 g, 4.0 mmol), Me_2Zn (3 ml of 2M solution in hexane, 6.0 mmol) and $TMEDA$ (0.47 g, 4.0 mmol); yield 1.42 g, 87 %, mp 97-99°C. Analysis found (calc. for $C_{11}H_{19}F_7N_2O_2Zn$): C 32.2 (32.4), H 4.5 (4.7), N 6.9 (6.9) %. 1H NMR (300 MHz, THF- d^8) δ ppm: 2.69 (s, 4H, NCH_2), 2.45 (s, 12H, NCH_3), -0.93 (s, 3H, $ZnCH_3$), ^{13}C NMR (500 MHz, THF- d^8) δ ppm: 161.7 (t, 25.1 Hz,

CO₂), 119.3 (qt, $J = 286.6, 33.8$ Hz, CF₃), 110.2 (tsxt, $J = 264.8, 36.0$ Hz, CF₂CF₃), 109.8 (tt, $J = 263.8, 31.6$ Hz, O₂CCF₂), 57.8 (s, NCH₂), 47.0 (s, NCH₃), -18.7 (s, ZnCH₃), ¹⁹F NMR (400MHz, THF- d^8) δ ppm: -83.6 (CF₃), -119.9 (CF₂), -129.4 (CF₂)

EtZn(O₂CC₂F₅)TMEDA (11): Using C₂F₅COOH (0.65 g, 4.0 mmol), Et₂Zn (6 ml of 1M solution in hexane, 6.0 mmol) and TMEDA (0.47 g, 4.0 mmol); yield 1.36 g, 91 %. On standing, crystals formed in oil. Analysis found (calc. for C₁₁H₂₁F₅N₂O₂Zn): C 35.3 (35.5), H 5.6 (5.7), N 7.5 (7.5) %. ¹H NMR (300 MHz, THF- d^8) δ ppm: 2.68 (s, 4H, NCH₂), 2.45 (s, 12H, NCH₃), 1.18 (t, $J = 8.10$ Hz, 3H, ZnCH₂CH₃), 0.10 (q, $J = 8.30$ Hz, 2H, ZnCH₂CH₃), ¹³C NMR (300 MHz, THF- d^8) δ ppm: 162.2 (t, 26.1 Hz, CO₂), 120.2 (qt, $J = 284.7, 34.7$ Hz, CF₃), 108.2 (tq, $J = 262.4, 37.2$ Hz, CF₂), 57.8 (s, NCH₂), 47.1 (s, NCH₃), 13.4 (s, ZnCH₂CH₃), -3.3 (s, ZnCH₂CH₃), ¹⁹F NMR (400MHz, THF- d^8) δ ppm: -85.5 (CF₃), -122.6 (CF₂)

EtZn(O₂CC₃F₇)TMEDA (12): Using C₃F₇COOH (0.86 g, 4.0 mmol), Et₂Zn (6 ml of 1M solution in hexane, 6.0 mmol) and TMEDA (0.47 g, 4.0 mmol); yield 1.51 g, 89 %. Analysis found (calc. for C₁₂H₂₁F₇N₂O₂Zn): C 33.9 (34.1), H 4.9 (5.0), N 6.5 (6.4) %. ¹H NMR (300 MHz, THF- d^8) δ ppm: 2.68 (s, 4H, NCH₂), 2.46 (s, 12H, NCH₃), 1.18 (t, $J = 8.10$ Hz, 3H, ZnCH₂CH₃), 0.09 (q, $J = 8.30$ Hz, 2H, ZnCH₂CH₃), ¹³C NMR (500 MHz, THF- d^8) δ ppm: 161.6 (t, $J = 24.5$ Hz, CO₂), 119.3 (qt, $J = 287.0, 34.5$ Hz, CF₃), 110.2 (tsxt, $J = 264.3, 36.1$ Hz, CF₂CF₃), 108.2 (tt, $J = 264.3, 30.9$ Hz, O₂CCF₂), 57.8 (s, NCH₂), 47.1 (s, NCH₃), 13.3 (s, ZnCH₂CH₃), -3.3 (s, ZnCH₂CH₃), ¹⁹F NMR (400MHz, THF- d^8) δ ppm: -83.6 (CF₃), -119.8 (CF₂), -122.6 (CF₂)

Synthesis of [Zn(O₂CC₂F₅)₂TMEDA]₂ (13): C₂F₅COOH (1.30 g, 8.0 mmol) was added to a stirred solution of Et₂Zn (4 ml of 1M solution in hexane, 4.0 mmol) and TMEDA (0.47 g, 4.0 mmol) in hexane (10 ml) at -78 °C. Solution was stirred overnight while slowly warming up to room temperature. Solvent and volatiles were removed *in vacuo*, a white solid remained. Solid was redissolved in THF (5 ml) and colourless crystals were obtained on cooling to -20°C (1.74 g, 86 %, mp 97-99 °C). Analysis found (calc. for C₁₂H₁₆F₁₀N₂O₄Zn): C 28.3 (28.4), H 3.1(3.2), N 5.5 (5.5) %. ¹H NMR (300 MHz, THF- d^8) δ ppm: 2.73 (s, 4H, NCH₂), 2.50 (s, 12H, NCH₃), ¹³C NMR (300 MHz, THF- d^8) δ ppm: 162.7 (t, $J = 26.7$ Hz, CO₂), 119.8 (qt, $J = 285.9, 34.7$ Hz, CF₃), 108.1 (tq, $J = 263.0, 37.8$ Hz, CF₂), 57.5 (s, NCH₂), 46.8 (s, NCH₃), ¹⁹F NMR (400MHz, THF- d^8) δ ppm: -85.7 (CF₃), -123.1 (CF₂)

Also prepared by the same method:

$[Zn(O_2CC_3F_7)_2TMEDA]_2$ (**14**): Using C_3F_7COOH (1.71 g, 8.0 mmol), Et_2Zn (4 ml of 1M solution in hexane, 4.0 mmol) and TMEDA (0.47 g, 4 mmol); yield 2.05 g, 85 %, mp 119-120 °C. Analysis found (calc. for $C_{14}H_{16}F_{14}N_2O_4Zn$): C 27.8 (27.7), H 2.5 (2.7), N 4.7 (4.6) %. 1H NMR (500 MHz, THF- d^8) δ ppm: 2.72 (s, 4H, NCH_2), 2.49 (s, 12H, NCH_3) ^{13}C NMR (500 MHz, THF- d^8) δ ppm: 162.8 (br. s, CO_2), 119.1 (qt, $J = 287.0$, 34.5 Hz, CF_3), 110.0 (tsxt, $J = 266.1$, 36.1 Hz, CF_2CF_3), 109.8 (tt, $J = 265.2$, 37.1 Hz, O_2CCF_2), 57.7 (s, NCH_2), 47.0 (s, NCH_3), ^{19}F NMR (500MHz, THF- d^8) δ ppm: -83.8 (t, $J = 8.67$ Hz, CF_3), -120.6 (br. s, CF_2), -129.6 (s, CF_2).

Recrystallization of **14** from THF produced a few crystals of the hydrated species

$[Zn(O_2CC_3F_7)_2TMEDA]_2 \cdot H_2O$ (**15**), which has been characterised solely by X-ray crystallography.

Crystallography

Experimental details relating to the single-crystal X-ray crystallographic studies are summarised in Table 1. For all structures, data were collected on a Nonius Kappa CCD diffractometer at 150(2) K using Mo- K_α radiation ($\lambda = 0.71073$ Å). Structure solution was followed by full-matrix least squares refinement and was performed using the WinGX-1.70 suite of programmes.²³ There were several issues with the structure determinations, specifically associated with disorder in the fluorocarbon groups, details of which are given below; in no case is the overall structure compromised by the difficulties in addressing these disorders.

In **2**, there are two Zn_5 units linked through an inversion centre at the heart of the dimer. Two of the C_2F_5 groups show disorder, one in the ratio 50:50 and the other in the ratio 70:30; two internuclear distances [$C(4)$ - $F(2)$ and $C(7)$ - $F(7A)$] have been restrained.

Difficulties in solving and refining the structure of **8** were concentrated at the 'determination of space group'. The absences recorded were indicative of 3 possibilities viz. $Pnm2_1$, $Pn21m$ and $Pnmm$, none of which afforded a reasonable starting point. Ultimately, the structure was solved in a low symmetry space group, and the location of the motif used to establish the correct assignment ($P22_12_1$) as presented herein. The employment of special positions invoked in the model, give rise to a special absence – in this case the ' n ' glide - which is not 'real'. Refinement was uneventful, and residual electron density is chemically insignificant, being a ripple close to one of the zinc atoms in the aggregate that constitutes the core of this compound.

Table 1. Crystal data and structure refinement for **2**, **5–8**, **11**, **13**, **15**.^a

	2	5	6	7	8	11	13	15
Empirical formula	C ₄₄ H ₂₄ F ₆₀ O ₂₈ Zn ₁₀	C ₁₀ H ₁₀ F ₁₀ O ₄ Zn ₂	C ₄₀ H ₁₀ F ₆₀ O ₂₆ Zn ₉	C ₆ H ₅ F ₇ O ₂ Zn	C ₄₀ H ₄₀ F ₄₂ O ₁₇ Zn ₈	C ₁₁ H ₂₁ F ₅ N ₂ O ₂ Zn	C ₂₄ H ₃₂ F ₂₀ N ₄ O ₈ Zn ₂	C ₂₈ H ₃₄ F ₂₈ N ₄ O ₉ Zn ₂
Formula weight	2794.33	514.92	2634.81	307.47	2113.68	373.67	1015.28	1233.33
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic	Triclinic
Space group	P2 ₁ /n	P $\bar{1}$	C2/c	C2/c	P22 ₁ 2 ₁	P2 ₁ /n	Pc2 ₁ b	P $\bar{1}$
<i>a</i> (Å)	10.3599(4)	9.5320(7)	20.1556(5)	19.1655(8)	13.260(2)	8.5671(2)	12.6211(2)	9.7929(2)
<i>b</i> (Å)	20.8103(10)	9.7246(6)	17.4860(5)	10.4966(4)	13.903(2)	15.6795(5)	16.2796(2)	15.4901(3)
<i>c</i> (Å)	19.4299(10)	10.1299(9)	23.4712(5)	10.0172(3)	18.434(3)	12.7444(3)	19.1244(3)	15.5496(4)
α (°)		62.429(5)						95.574(1)
β (°)	97.699(3)	86.995(4)	112.553(1)	102.881(3)		109.487(1)		104.898(1)
γ (°)		88.439(4)						96.891(1)
<i>V</i> (Å ³)	4151.2(3)	831.21(11)	7639.6(3)	1964.47(13)	3398.5(9)	1613.86(7)	3929.42(10)	2242.78(9)
<i>Z</i>	2	2	4	8	2	4	4	2
ρ_{calc} (mg m ⁻³)	2.236 3	2.057	2.291	2.079	2.066	1.538	1.716	1.826
$\mu(\text{Mo-K}\alpha)$ (mm ⁻¹)	3.041	3.004	2.992	2.589	2.947 [†]	1.577	1.362	1.237
<i>F</i> (000)	2704	504	5072	1200	2068	768	2032	1228
Crystal size (mm)	0.10x0.10x0.10	0.45x0.20x0.10	0.15x0.10x0.05	0.45x0.10x0.10	0.20x0.20x0.15	0.40x0.35x0.25	0.50x0.50x0.40	0.30x0.30x0.30
Theta range (°)	3.62 - 25.03	5.18 - 24.97	3.68 - 27.51	3.21 - 27.46	3.58 - 27.46 ^o	4.35 - 27.49	4.61 - 27.45	2.94 - 27.54
Refl'ns collected	41678	7439	65172	17749	26448	20503	52992	45149

Independent refl'ns [R(int)]	7213 [0.3187]	2874 [0.0627]	8731 [0.1223]	2238 [0.0503]	7744 [0.0808]	3677 [0.0376]	8910 [0.0515]	10254 [0.0619]
Refle'ns observed (>2 σ)	4200	2321	4916	1752	5934	3177	7608	6782
Data Completeness	0.982	0.984	0.993	0.996	0.994	0.992	0.992	0.990
max min trans		0.7532,0.3450	0.8648,0.6624	0.7818,0.3887	0.5533,0.3412	0.6939,0.5712	0.6118,0.5491	0.7078,0.7078
Goodness-of-fit on F ²	1.073	1.063	1.021	1.052	1.074	1.084	1.037	1.018
Final R ₁ , wR ₂ [I>2 σ (I)]	0.0736,0.1702	0.0831,0.2256	0.0569,0.0978	0.0317,0.0729	0.0748,0.1999	0.0303,0.0712	0.0374, 0.0941	0.0472,0.1073
Final R ₁ , wR ₂ (all data)	0.1422,0.2132	0.0982,0.2430	0.1310,0.1210	0.0503,0.0808	0.0934,0.2114	0.0381,0.0769	0.0487,0.1027	0.0890,0.1254
Largest diff. peak, hole (eÅ ⁻³)	1.081,-1.113	3.859, -1.026	0.650, -0.609	0.472,-0.571	3.035, -1.103	0.384,-0.372	0.424,-0.376	0.917,-0.708
Flack parameter					0.02(2)		0.007(11)	

In **13** there is disorder in two out of the four C₂F₅ groups in the ratio 1:1. There is potential disorder in one more C₂F₅ group, however it was not possible to resolve this; in particular, C(21) has a very large ADP and could potentially be split into two positions but attempts to effect this resulted in divergent refinement. All internuclear distances in the disordered groups have been idealised and some of the ADPs equalised. In **15** there is disorder in two of the four C₃F₇ groups in the ratio 60:40. All C-C and some C-F internuclear distances in the disordered C₃F₇ group based on C(31)-C(34) have been restrained. The hydrogen atoms of the water ligand have been located in the difference Fourier map and freely refined.

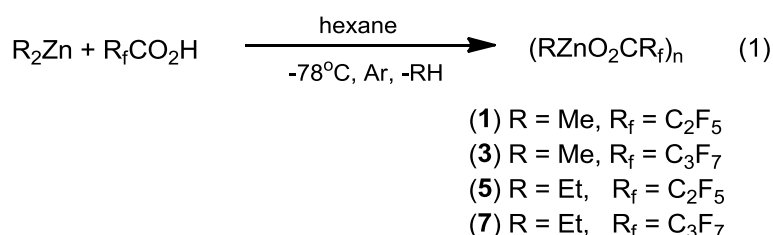
Materials Chemistry

TGA Analysis of the complexes was performed using a Perkin Elmer TGA 4000 Thermogravimetric Analyzer. Data points were collected every second at a ramp rate of 20 °C min⁻¹ in a flowing (50 mL min⁻¹) N₂ stream. CVD was carried out on an ElectroGas Systems cold-walled reactor with associated gas lines and electronic heater controls. Specific conditions used for precursors **3**, **10**, **13** were: **3**: Films were grown at 450°C onto glass for 2 hours with the line and bubbler temperatures set to 150°C and a pressure of 47.2 Torr; **10**: Films were grown on glass substrates at a reactor temperature of 400°C, with a line and bubbler temperature of 90°C and a pressure of 39.6 Torr for a duration of 90 mins; **13**: Films were grown on glass substrates at a reactor temperature of 450°C and a bubbler and line temperature of 150°C for 120 minutes at a pressure of 39.8 Torr. In all cases, there was a bleed of mixed N₂ (300 mL min⁻¹) and O₂ (60 mL min⁻¹) as carrier gas.

Results and Discussion

Synthesis and Structures

Organozinc fluorocarboxylates were prepared following a literature method for the preparation of EtZnO₂CPh (Eqn. 1).²⁴ The resulting air- and moisture-sensitive white products were isolated and characterized by NMR, which are unexceptional save that they confirm the retention of one alkyl group on zinc and, from the ¹³C NMR, that the fluorocarbon residue remains intact; yields were in the range 61 – 70 %



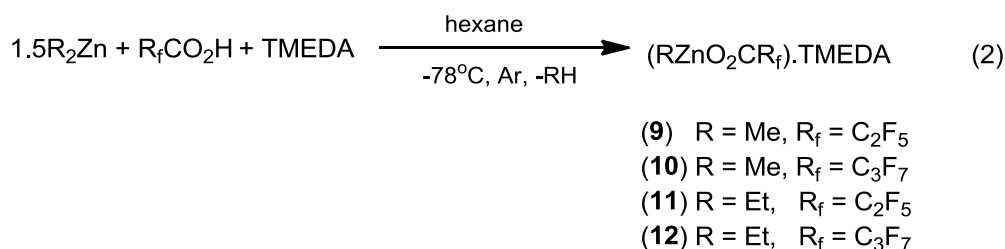
Initial attempts to recrystallize (**1**) and (**3**) by adding CH₂Cl₂ to the hexane solution and cooling to -20°C produced two oxidation products, Zn₁₀Me₄(OMe)₄(O₂CR_f)₁₂ [R_f = C₂F₅ (**2**); C₃F₇ (**4**)]. Both (**2**) and (**4**) showed ¹H NMR resonances due to the different ZnMe and ZnOMe peaks with shifts of -0.81, 3.44 ppm (**2**) and -0.84, 3.52 ppm (**4**) in a 1 : 1 ratio. The presence of OMe groups is consistent with a reaction of **1**, **3** with O₂, as the reaction between O₂ and dialkylzinc compounds is known to produce first zinc peroxides which then transform to the thermodynamically more stable alkoxides.²⁵⁻²⁷

Similarly, a small number of crystals of Zn₉Et₂(O₂CC₂F₅)₁₂(O)₂ (**6**) were obtained from dissolving the hexane insoluble precipitate left from the synthesis of **5** in a hexane/CH₂Cl₂ mixture and cooling to -20°C, though the amount of material was sufficient only for crystallography and microanalysis. The inclusion of oxygen atoms within the cage could be plausibly attributed to two different mechanisms. Lewiński *et al.* have synthesised a similar cage, [Zn(O₂CPh)]₄O, on addition of dry O₂ to [EtZn(O₂CPh)]_n. They speculated that the mechanism starts with attack of O₂ on the Zn-C bond to form a peroxide, EtOOZn(O₂CPh), which could then associate with any remaining [EtZn(O₂CPh)]_n to form [EtZn(O₂CPh)]_x[EtOOZn(O₂CPh)]_y. Homolysis of the O-O bond then produces both alkoxyl and oxyzinc radicals and the latter is the origin of the Zn-O-Zn moiety in the final product.²⁵⁻²⁶ Alternatively, **6** could simply be a product from the hydrolysis of **5**. **6** can also be reformulated as (EtZnL)₂(ZnL₂)₅(ZnO)₂ (L = O₂CC₂F₅) and it is possible that in solution **5** undergoes Schlenk equilibria to form a mixture of EtZnO₂CC₂F₅, Et₂Zn and Zn(O₂CC₂F₅)₂, with which a small amount of water in the solvent would hydrolyse Et₂Zn to form ZnO which is trapped by the remaining species; Schlenk equilibrium of this type are common for alkylzinc alkoxides.²⁶ The controlled hydrolysis of EtZn₂(O₂CR)₃(THF) to form Zn₄(O)(O₂CR)₆ has recently been reported.⁸

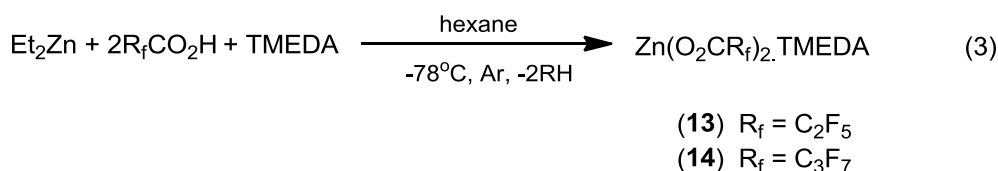
Finally, Zn₈Et₄(OEt)₄(O₂CC₃F₇)₆(O) (**8**) was obtained from initial attempts to recrystallize **7** from the addition of CH₂Cl₂ to the hexane solution and cooling to -20°C. Although the structure itself is very different to that of **6** it is likely that a similar mechanism is involved in its formation i.e. reaction **7** with either O₂ or water. The ¹H spectrum of **8** shows the EtZn and ZnOEt groups [¹H δ of -0.01 (2H, ZnCH₂), 0.96 (3H, ZnCH₂CH₃), 1.07 (3H, OCH₂CH₃) and 3.74 ppm (2H, OCH₂)] while the ¹³C NMR includes the expected coupling between ¹⁹F and ¹³C of the R_f ligand.

In order to influence the volatility of the organozinc fluorocarboxylates, their synthesis was repeated in the presence of tetramethylethylenediamine (TMEDA) to attempt to break up the polymeric structures of the former (*see below*). Thus, 1: 1 adducts **9** - **12** were synthesised in the reaction between R₂Zn (R = Me, Et) and R_fCO₂H (R_f = C₂F₅, C₃F₇) in the presence of TMEDA in hexane, using a slight excess of R₂Zn to ensure

all the carboxylic acid reacted (Eqn. 2). Volatiles were removed *in vacuo*, yielding the desired products as oils, though in the case of **11** this crystallized on standing over several days. ¹H NMR showed the correct 1:1 stoichiometry of alkylzinc species to TMEDA ligand.



TMEDA adducts of zinc fluorocarboxylates Zn(O₂CR_f)₂·TMEDA were similarly synthesized from the reaction between Et₂Zn and two equivalents of fluorocarboxylic acid in the presence of TMEDA in hexane (Eqn. 3). ¹H and ¹³C NMR confirmed the presence of TMEDA and the carboxylate ligand, respectively.



Crystals of [Zn(O₂CC₃F₇)₂·TMEDA]₂·H₂O (**15**) were also obtained on cooling a solution of **14** in THF to -20°C over a period of 3 months.

Structural Analysis

The structures of RZnO₂CR_f (R = Et, R_f = C₂F₅ **5**, C₃F₇ **7**) have been determined and are essentially the same; a twined crystal of **1** (R = Me, R_f = C₂F₅) was also studied, and although a complete structure determination could not be completed, the data were sufficient to show that it also adopts the same structure as both **5** and **7**. Accordingly, only data for **7** is discussed here, with details for **5** available as supplementary data.

The structure of EtZnO₂CC₂F₇ (**5**) (Fig. 1) is that of a polymeric chain in which each carboxylate ligand bridges two zinc atoms. In addition, O(1) of the ligand bridges two zinc atoms in a μ₂ manner, such that [EtZnO₂CC₂F₅]₂ dimers are joined *via* four-membered Zn₂O₂ rings. There is one long and one short Zn-O interaction, the shorter one involving the singly bridging-oxygen atoms [Zn-O(2): 1.9853(17) Å] with the longer Zn-O contacts belonging to the μ₂-oxygen atoms [Zn-O(1): 2.1528(17), Zn-O(1') 2.1634(16) Å]. Although zinc is nominally four-coordinate, bond angles around the metal lie in the range 77.40(7) - 140.15(10) °, a degree of distortion which could be due to the close intermolecular contact with F(2)

[2.789(16) Å]. This separation is longer than the sum of the covalent radii (2.04 Å) but shorter than the sum of the van der Waals radii (2.91 Å).

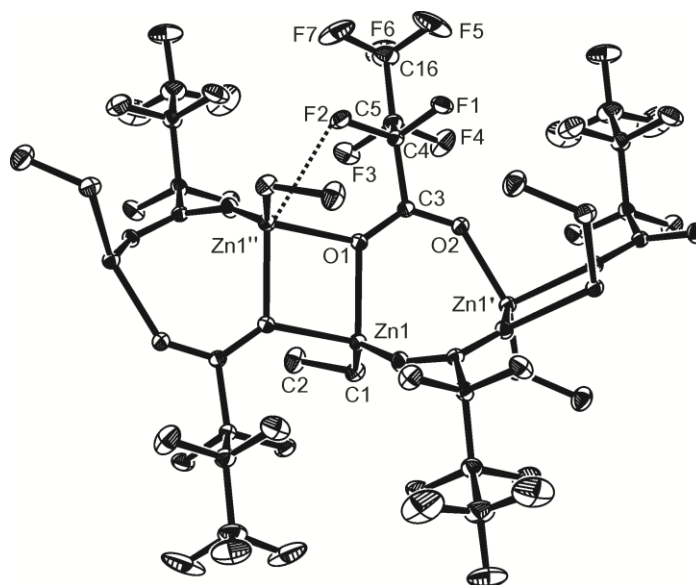


Figure 1: The asymmetric unit of **7** showing the labelling scheme used in the text and tables; thermal ellipsoids are at the 25 % level. The figure shows a section of the polymer chain propagating along *c*. Selected geometric data: Zn-C(1) 1.939(3), Zn-O(1) 2.1528(17), Zn-O(2) 1.9853(17), Zn-O(1') 2.1634(16), Zn...F(2) 2.789(16), O(1)-C(3) 1.262(3), O(2)-C(3) 1.237(3) Å; C(1)-Zn-O(1) 117.20(10), C(1)-Zn-O(2) 140.15(10), C(1)-Zn-O(1) 115.45(9), O(1)-Zn-O(2) 94.76(7), O(1)-Zn-O(1) 77.40(7), O(2)-Zn-O(1') 93.26(7) °. Symmetry operations: ' -*x*, *y*, 1/2-*z*; '' -*x*, -*y*, -*z*.

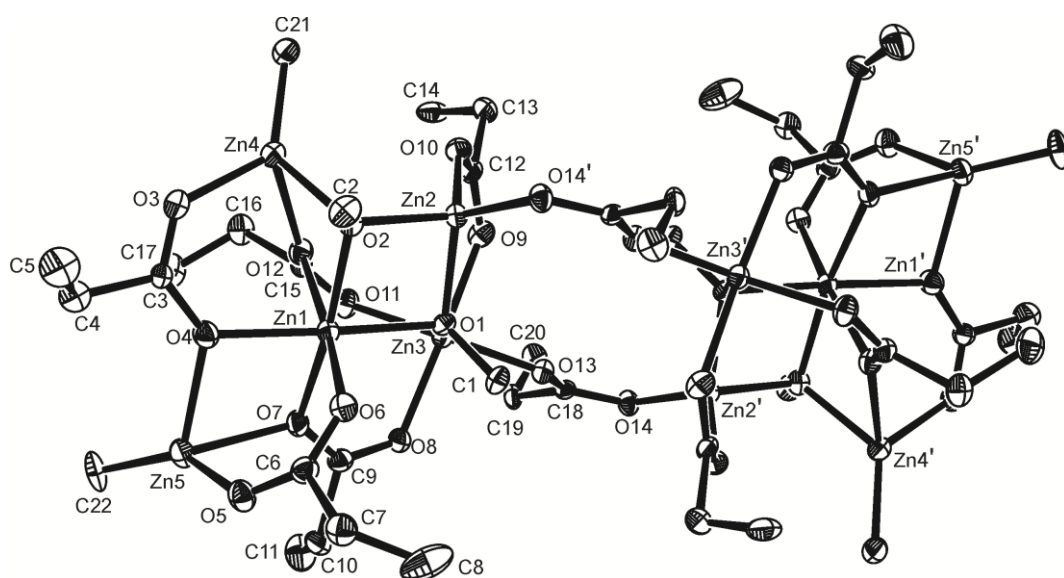
Four other $RZnO_2CR'$ structures free from additional donor groups have been reported which have lower degrees of oligomerization than those of **1**, **5**, **7**, namely hexameric $EtZnO_2CPh$,²⁴ tetrameric $C_6F_5ZnO_2CR'$ (R' = mesityl, 2- ClC_6H_4)⁶ and dimeric when *R* is the extremely bulky *m*-terphenyl.²⁸ A more direct comparison can be made with the polymeric nature of $EtZnO_2CCH_3$ ³ although here a sheet structure is adopted in which Zn_2O_2 rings are linked by 16-membered $[Zn(O_2CCH_3)]_4$ tetramers rather than the $[Zn(O_2CR_f)]_2$ dimers seen in **7** *et al.*

The simple $RZnO_2CR_f$ are very sensitive to either O_2 and/or H_2O , and react to yield the Zn_{10} (**2**, **4**), Zn_9 (**6**) and Zn_8 (**8**) aggregated products. As far as we are aware, Zn_7 clusters, e.g. $Zn_7(O)_2(O_2CMe)_{10}(1-Meim)_2$ (1-Me-im = 1-methylimidazole)²⁹ are the largest comparable systems reported to date. Both **2** and **4** adopt

the same $\text{Zn}_{10}\text{Me}_4(\text{OMe})_4(\text{O}_2\text{CR}_f)_{12}$ formula, though disorder in the C_3F_7 groups in **4** hindered full structural determination, but it adopts the same framework as that of **2** (Fig. 2).

The structure of **2** (Fig. 2a) consists of a cage of five zinc atoms, surrounded by six bridging carboxylate ligands, two OMe groups and two Me groups; one of the carboxylate ligands [based on C(18)] bridges to a symmetry-related second Zn_5 cage to yield an overall Zn_{10} aggregate. Of the five zinc atoms, Zn(1) is in the centre of the cage and is six-coordinated in a ZnO_6 environment, exhibiting a slightly distorted structure with bond angles ranging from $80.7(3)^\circ$ – $101.6(3)^\circ$ between adjacent atoms and $168.1(3)^\circ$ – $174.7(3)^\circ$ between opposite atoms. Of the remaining four zinc atoms, Zn(3) is five-coordinate ZnO_5 and Zn(2), Zn(4) and Zn(5) are all four-coordinate though the first of these has ZnO_4 coordination and the latter pair bear methyl groups and are ZnCO_3 in ligation. A simplified view of the Zn_5 core is shown in Fig. 2b.

Five-coordinate Zn(3) exhibits very distorted geometry (τ value of 0.42),³⁰ which is roughly half way between square-based pyramid and trigonal bipyramidal geometry. Zn(2), Zn(4) and Zn(5) all exhibit distorted tetrahedral geometry, with a much higher degree of distortion seen in Zn(4) and Zn(5), with bond angles ranging from $88.6(3)^\circ$ - $114.7(3)^\circ$, $76.2(3)^\circ$ - $129.7(4)^\circ$ and $75.9(3)^\circ$ – $143.6(5)^\circ$ respectively.



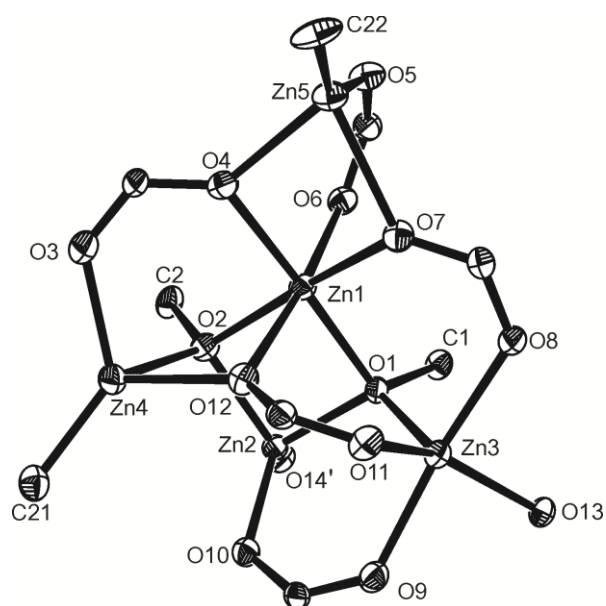


Figure 2: (a, top) The asymmetric unit of **2** showing the labelling scheme used in the text and tables and (b, bottom) a simplified view of the Zn₅ core; thermal ellipsoids are at the 25 % level. Fluorine atoms have been removed for clarity. Selected internuclear distances: Zn(1)-O(1) 2.095(7), Zn(1)-O(2) 2.081(8), Zn(1)-O(4) 2.103(7), Zn(1)-O(6) 2.010(8), Zn(1)-O(7) 2.107(8), Zn(1)-O(12) 2.180(8), Zn(2)-O(1) 1.995(7), Zn(2)-O(2) 1.986(7), Zn(2)-O(10) 1.923(8), Zn(2)-O(14') 1.932(7), Zn(3)-O(1) 2.023(7), Zn(3)-O(8) 2.056(8), Zn(3)-O(9) 2.071(9), Zn(3)-O(11) 2.035(7), Zn(3)-O(13) 2.014(7), Zn(4)-O(2) 2.090(7), Zn(4)-O(3) 2.026(8), Zn(4)-O(12) 2.207(8), Zn(4)-C(21) 1.931(13) Å. Symmetry operation: 1-x, -y, -z.

All the carboxylate groups bridge over at least two zinc atoms; of the six unique carboxylate ligands two bridge between zinc atoms within the Zn₅ unit [those based on C(6), C(12)], three have an additional μ_2 -link between two metals [i.e. coordinate three Zn in total; ligands based on C(3), C(9) and C(15)], while the final carboxylate [involving C(18)] bridges between Zn₅ moieties. The singly-bridging oxygen atoms have interatomic distances that range from 1.923(8) Å – 2.071(9) Å while the μ_2 -oxygen atoms have slightly longer interatomic distances, ranging from 2.103(7) Å – 2.258(7) Å. The oxygens of the OMe groups bridge in a μ_3 mode over three zinc atoms, Zn(1), Zn(2) and Zn(3) in the case of O(1) and Zn(1), Zn(2) and Zn(4) in the case of O(2). The Zn-O interatomic distances range from 1.986(7) Å – 2.095(7) Å, within the same range as the singly bridging oxygen atoms of the carboxylate groups and slightly shorter than the μ_2 -oxygen atoms.

Both Me groups are bonded to only one zinc atom each [Zn(4) and Zn(5)] and sit on the outskirts of the cage.

As far as we are aware, the Zn_{10} framework of **2** and **4** are unique, but are clearly related to three known $Zn_5R_4(O_2CR')_6$ species ($R = Et$, $R' = Me$;³¹ $R = C_6F_5$, $R' = 2,4,6-Me_3C_6H_2$, $3-Me_2NC_6H_4$)⁶ in that (i) there has been oxygen insertion into two Zn-R bonds of such species and (ii) the Zn_5 units in these compounds are now linked by one bridging carboxylate from each unit in **2**, **4**.

The nona-zinc species $Zn_9Et_2(O_2CC_2F_5)_{12}(O)_2$, (**6**) (Fig. 3) contains a six-coordinate ZnO_6 [Zn(1)] which sits on an inversion centre about which the cluster is built. **6** contains two other ZnO_6 moieties [Zn(4), Zn(4')] and six four-coordinate zinc species, of which four have a ZnO_4 environment [Zn(2), Zn(3) and their symmetry-related partners] and two are $ZnCO_3$ species [Zn(5), Zn(5')], which are the ethylzinc moieties at the two ends of the molecule. In contrast to **2** and **4**, the carboxylate groups in **6** are predominantly O,O-bridging between two zinc atoms with one end also acting in a μ_2 -manner generating Zn-O-Zn linkages [eight, based on C(1), C(4), C(7), C(13) and symmetry-related groups], while only four ligands act purely in an O,O-bridging mode [based on C(10), C(16) and their partners]. Finally, O(13) acts in a μ_4 -manner linking Zn(1) – Zn(4) inclusive. Of the two six-coordinate Zn atoms, Zn(1) exhibits a geometry which is much closer to a perfect octahedron with bond angles of 180.0° between opposite oxygen atoms and bond angles in the range $80.19(13)^\circ - 99.81(13)^\circ$ between adjacent oxygen atoms. Zn(4) shows a much more distorted geometry for which the corresponding ranges of angles are $154.92(15)^\circ - 178.03(15)^\circ$ and $74.36(13)^\circ - 103.57(14)^\circ$ respectively. Of the four-coordinate zinc atoms, Zn(5) shows much more distortion [bond angles range: $73.01(14)^\circ - 135.2(2)^\circ$] than either Zn(2) and Zn(3) [bond angles: $98.20(18)^\circ - 113.81(15)^\circ$ and $99.31(18)^\circ - 113.78(15)^\circ$, respectively]. The singly-bridging oxygen atoms have Zn-O interatomic distances that range from $1.938(4) \text{ \AA} - 1.983(4) \text{ \AA}$, while the μ_2 oxygen atoms have longer Zn-O interatomic distances [$2.101(4) - 2.454(4) \text{ \AA}$]; the oxygen atom in the centre of the molecule, O(13), bridges over four Zn atoms and has Zn-O interatomic distances that are within the same range as the singly bridging carboxylate oxygen atoms [$1.937(3) \text{ \AA} - 1.995(3) \text{ \AA}$].

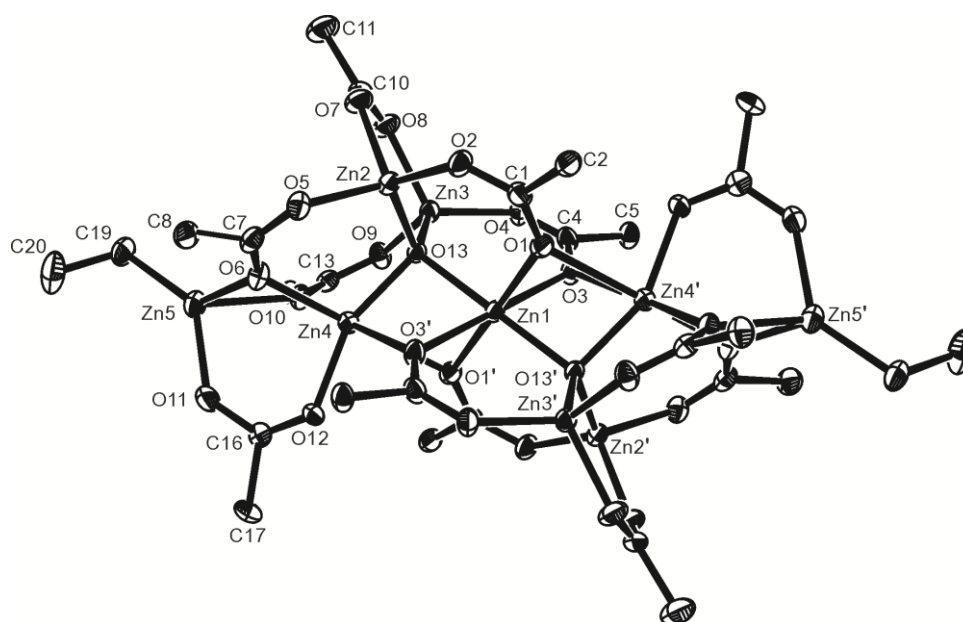


Figure 3: The asymmetric unit of **6** showing the labelling scheme used in the text and tables; thermal ellipsoids are at the 25 % level. Only the α -carbon of the C_2F_5 groups have been included for clarity; C(18) is hidden behind O(10). Selected internuclear distances: Zn(1)-O(1) 2.173(4), Zn(1)-O(3) 2.172(4), Zn(1)-O(13) 1.995(3), Zn(2)-O(2) 1.942(4), Zn(2)-O(3) 1.978(4), Zn(2)-O(7) 1.955(4), Zn(2)-O(13) 1.937(3), Zn(4)-O(1') 2.423(4), Zn(4)-O(3) 2.454(4), Zn(4)-O(6) 2.108(4), Zn(4)-O(10) 2.101(4), Zn(4)-O(12) 1.938(4), Zn(4)-O(13) 1.940(3), Zn(5)-O(6) 2.270(4), Zn(5)-O(10) 2.236(4), Zn(5)-O(11) 1.950(5), Zn(5)-C(19) 1.924(6) Å. Symmetry operation: 1-x, 1-y, 1-z.

The asymmetric unit of octa-zinc $\text{Zn}_8\text{Et}_4(\text{OEt})_4(\text{O}_2\text{CC}_3\text{F}_7)_6(\text{O})$ (**8**) (Fig 4) is one half of the formula unit, the remainder generated by a two-fold axis through the μ_4 -O(1) at the centre of the cluster. The asymmetric unit of **8** comprises two five-coordinate ZnO_5 centers [Zn(1), Zn(2)] internal to the cluster and two four-coordinate ZnCO_3 units, which, as in **6**, are at the ends of the aggregate. In addition to the μ_4 -O(1), there are two μ_3 -OEt groups, two carboxylates which O,O-bridge and additionally link two metals in a μ_2 - manner through one oxygen [based on C(1), C(5)], and one carboxylate with is O,O-bridging only [based on C(9)]. Zn(1) and Zn(2) both adopt a distorted trigonal bipyramidal coordination and τ values³⁰ of 0.66 and 0.61 respectively. Zn(1) has two oxygens from the carboxylate groups in the axial positions [O(2) and O(7)] with one more carboxylate oxygen [O(3)], one oxygen from an OEt group [O(9)] and the central O(1) in the equatorial positions. Similarly, Zn(2) has O(4) and O(6) in axial positions, both from carboxylate groups, and the central O(1), O(8) from an OEt and O(5) from a carboxylate group in the equatorial positions. Zn(3) and

Zn(4) are both four-coordinate with a distorted tetrahedral structure and bond angles ranging from $78.9(2)^\circ$ – $130.8(5)^\circ$ and $79.4(2)^\circ$ – $130.8(4)^\circ$, respectively. The singly bridging oxygens all have similar Zn-O interatomic distances [$2.005(6)$ Å – $2.049(7)$ Å] and are similar to those involving the μ_3 -OEt ligands [$1.975(6)$ Å – $2.122(5)$ Å], while the μ_2 -oxygen atoms have longer Zn-O interatomic distances [$2.111(6)$ Å – $2.406(6)$ Å]. O(1) is in the centre of the cage, bridging over four zinc atoms with the two shortest Zn-O interactions [$1.955(4)$, $1.950(4)$ Å].

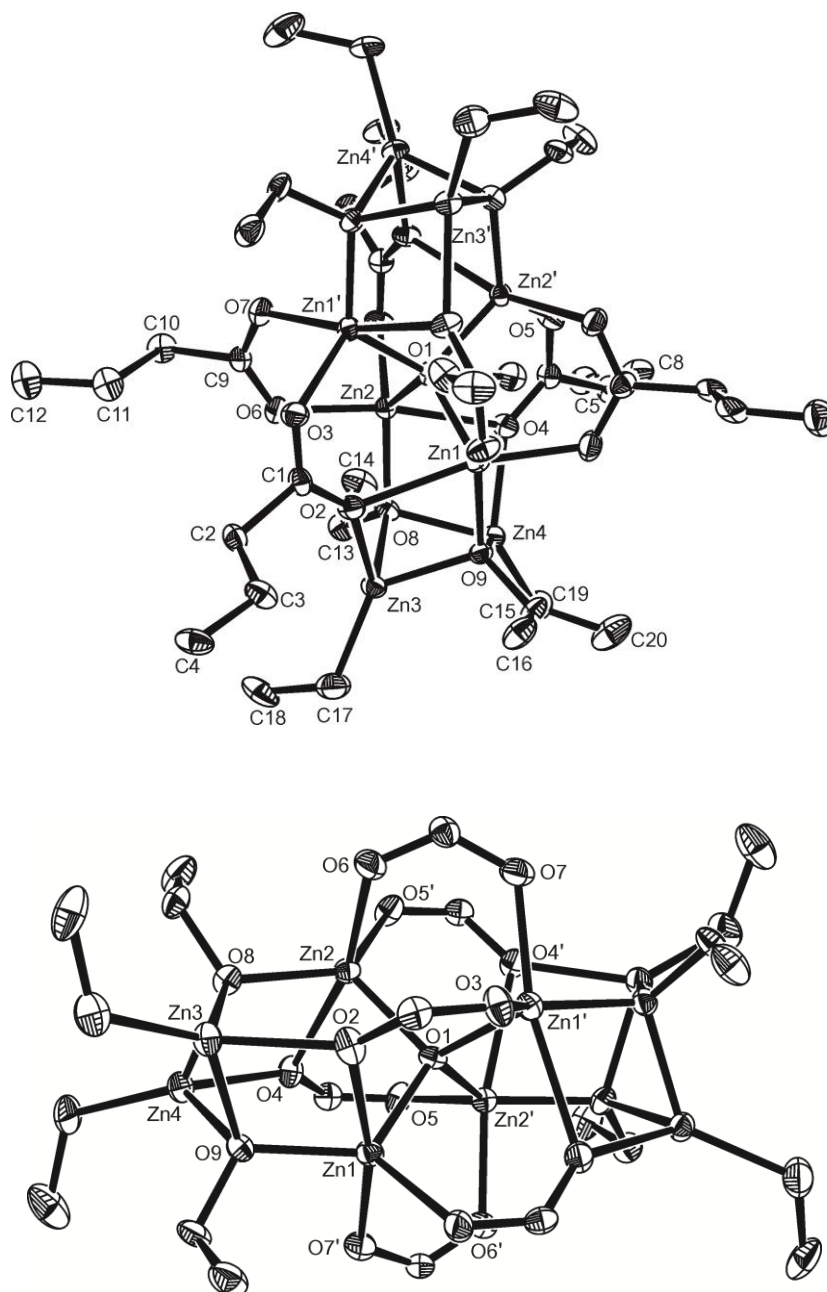


Figure 4: (a, top) The asymmetric unit of **8** showing the labelling scheme used in the text and tables; thermal ellipsoids are at the 25 % level. Fluorine atoms have been removed for clarity; C(6) and

C(7) are hidden by C(5); (b, bottom) the Zn_8O_{17} core of **8**. Selected internuclear distances Zn(1)-O(1) 1.955(4), Zn(1)-O(2) 2.406(6), Zn(1)-O(3') 2.017(6), Zn(1)-O(7') 2.049(7), Zn(1)-O(9) 1.975(6), Zn(3)-O(2) 2.113(6), Zn(3)-O(8) 2.122(5), Zn(3)-O(9) 2.066(6), Zn(3)-C(17) 1.991(12) Å. Symmetry operation: $x, 1-y, -z$.

The structure of $\text{EtZn}(\text{O}_2\text{CC}_2\text{F}_5)\cdot\text{TMEDA}$ **11** is monomeric in the solid state, with the carboxylate group showing monodentate coordination (Fig. 5); the Zn-O(2) bond [3.1341(16) Å] is outside the sum of the respective van der Waals radii (2.91 Å). The ligands are arranged about the central Zn atom in a distorted tetrahedral arrangement, with bond angles ranging from $84.86(6)^\circ$ [N(1)-Zn-N(2)] to $126.98(8)^\circ$ [C(10)-Zn-O(1)]. The TMEDA group shows iso-bidentate coordination, with identical internuclear distances between zinc and the two nitrogen atoms. Interestingly, despite the monodentate coordination of the carboxylate group, the internuclear distances between C(1) and both oxygen atoms are very similar, which can be rationalised by the presence of a weak hydrogen bond between O(2) and a hydrogen atom from an adjacent molecule [H(6b')]. The structure of $\text{EtZn}(\text{O}_2\text{CMe})(\text{C}_5\text{H}_4\text{N})$ has recently been determined³² and differs from **11** by incorporating a bridging carboxylate and a monodentate *N*-donor, though the coordination number at zinc is constant at four across both species.

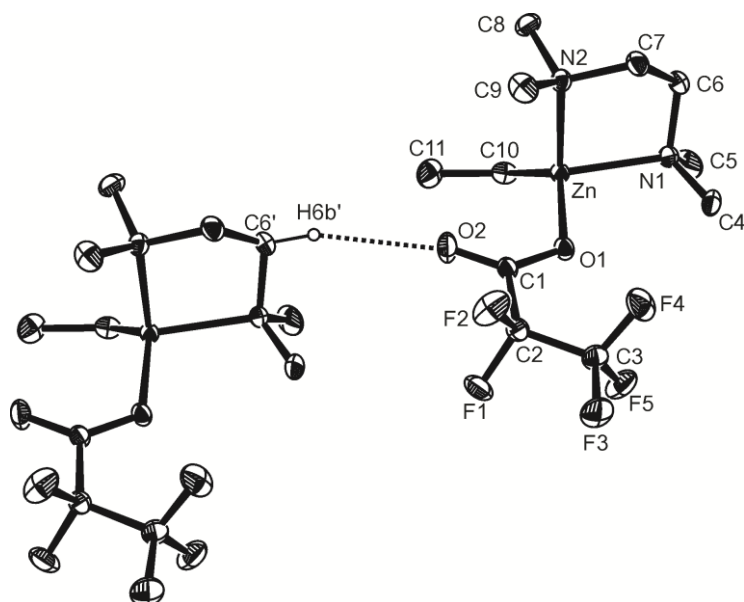


Figure 5: (a) The asymmetric unit of **11** showing the labelling scheme used in the text and tables; thermal ellipsoids are at the 25 % level. Selected geometric data: Zn-C(10) 1.977(2), Zn-O(1)

2.0102(13), Zn-N(1) 2.1388(17), Zn-N(2) 2.1409(16), O(1)-C(1) 1.262(2), O2-C(1) 1.213(2) Å; C(10)-Zn-O(1) 126.98(8), C(10)-Zn-N(1) 120.15(9), C(10)-Zn-N(2) 119.12(8), O(1)-Zn-N(1) 96.22(6), O(1)-Zn-N(2) 99.12(8), N(1)-Zn-N(2) 84.86(6) °; O(2)-H(6B') 2.54, C(6)...O(2) 3.484(3) Å, \angle C(6')-H(6B')...O(2) 160 °. Symmetry operation: x-1, y, z.

In contrast, $\text{Zn}(\text{O}_2\text{CC}_2\text{F}_5)\cdot\text{TMEDA}$ (**13**) forms a dimer with four carboxylate ligands bridging between the two zinc atoms with the two TMEDA ligands capping each end of the dimer; both metals adopt a distorted octahedral ZnO_4N_2 coordination (Fig. 6). All the carboxylate groups show bidentate coordination and in each case embody a short Zn-O to one metal and a longer, coordinate interaction with the other. There is minor difference in the behaviour of the two TMEDA ligands, with that bonded to Zn(1) TMEDA doing so in an iso-bidentate manner, while the TMEDA bonded to Zn(2) has slight asymmetry in the Zn-N internuclear distances. Of compounds of the same generic composition, only the structure of $\text{Zn}(\text{O}_2\text{CCH}_3)_2\cdot\text{TMEDA}$ structure appears to have been reported in literature and, in contrast to **13**, is monomeric with two aniso-bidentate acetate ligands and an iso-bidentate TMEDA ligand.³³

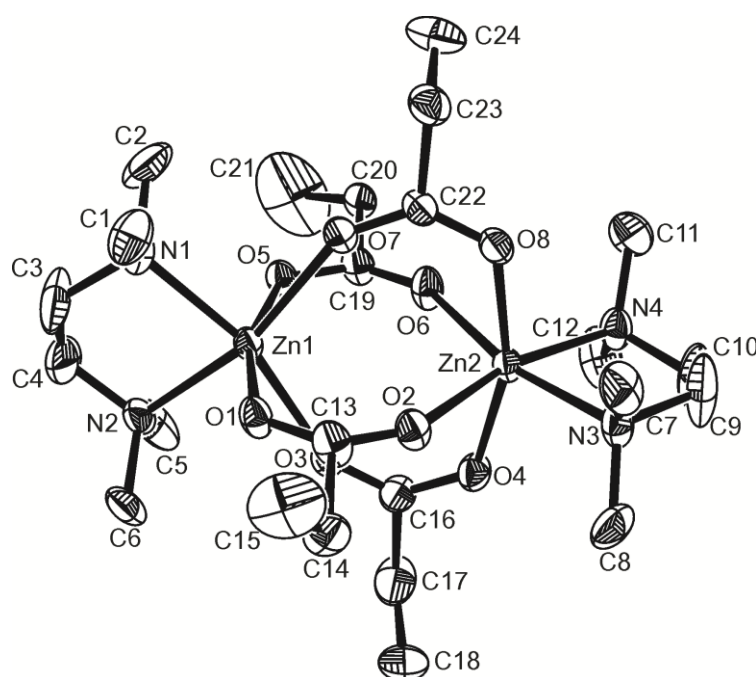


Figure 6: The asymmetric unit of **13** showing the labelling scheme used in the text and tables; thermal ellipsoids are at the 25 % level. Fluorine atoms have been removed for clarity; Selected geometric data for Zn(1) as typical of the two metal atoms: Zn(1)-O(1) 1.978(2), Zn(1)-O(3) 2.134(3), Zn(1)-O(5) 1.972(2), Zn(1)-O(7) 2.350(3), O(1)-C(13) 1.241(5), O(2)-C(13) 1.223(5),

O(3)-C(16) 1.220(5), O(4)-C(16) 1.249(5), Zn(1)-N(1) 2.185(3), Zn(1)-N(2) 2.199(3) Å; O(1)-Zn(1)-O(3) 84.82(12), O(1)-Zn(1)-O(5) 161.59(10), O(1)-Zn(1)-O(7) 85.02(11), O(1)-Zn(1)-N(1) 96.08(13), O(1)-Zn(1)-N(2) 98.31(12), O(3)-Zn(1)-O(5) 85.93(11), O(3)-Zn(1)-O(7) 113.71(9), O(3)-Zn(1)-N(1) 163.95(11), O(3)-Zn(1)-N(2) 80.99(12), O(5)-Zn(1)-O(7) 84.18(10), O(5)-Zn(1)-N(1) 97.20(13), O(5)-Zn(1)-N(2) 95.91(12), O(7)-Zn(1)-N(1) 82.32(12), O(7)-Zn(1)-N(2) 165.23(12), N(1)-Zn(1)-N(2) 83.03(14) °.

Prolonged crystallisation of $\text{Zn}(\text{O}_2\text{CC}_3\text{F}_7)\cdot\text{TMEDA}$ (**14**) yielded small amounts of crystals of the hydrate, $[\text{Zn}(\text{O}_2\text{CC}_3\text{F}_7)\cdot\text{TMEDA}]\cdot\text{H}_2\text{O}$ (**15**), which adopts the same structure as $[\text{Zn}(\text{O}_2\text{CCF}_3)\cdot\text{TMEDA}]\cdot\text{H}_2\text{O}$ reported by others.³⁴ While the overall dimeric nature and ZnO_4N_2 coordination is retained from **13**, the presence of a molecule of water, which bridges in a μ_2 -manner between metals, causes two of the carboxylate groups to become monodentate in **15** (Fig. 7). In turn, these are then engaged in intramolecular hydrogen bonding with the water molecule. The two bidentate carboxylate groups have very similar interatomic distances between the oxygen and the zinc, ranging from 2.078(2) – 2.097(2) Å while the two monodentate carboxylate groups have slightly longer bonds [Zn(1)–O(2) 2.143(2), Zn(2)–O(8) 2.127(2) Å]; the water molecule which bridges between the two zinc atoms has even longer Zn–O internuclear distances [Zn(1)–O(1) 2.184(2), Zn(2)–O(1). 2.205(2) Å].

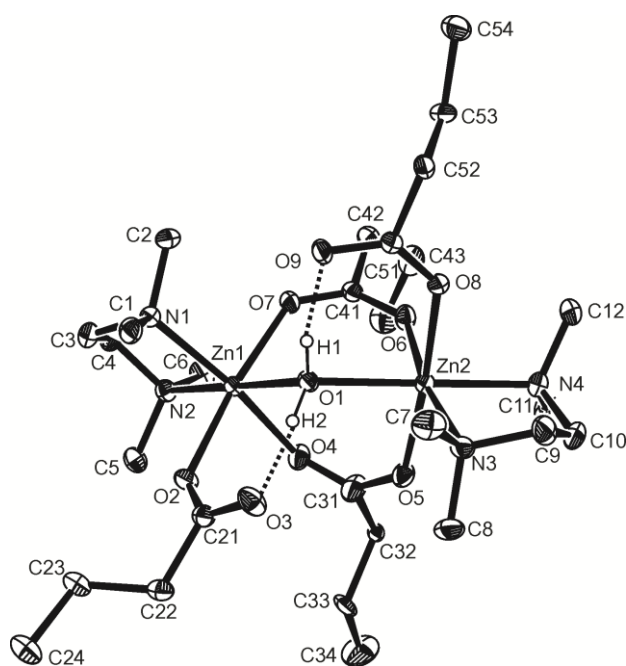


Figure 7: The asymmetric unit of **15** showing the labelling scheme used in the text and tables; thermal ellipsoids are at the 25 % level. Fluorine atoms have been removed for clarity; C(44) is hidden behind O(6). Selected geometric data for Zn(1) as typical of the two metal atoms: Zn(1)-O(1) 2.184(2), Zn(1)-O(2) 2.143(2), Zn(1)-O(4) 2.089(2), Zn(1)-O(7) 2.097(2), O(2)-C(21) 1.253(4), O(3)-C(21) 1.237(4), O(4)-C(31) 1.230(4), O(5)-C(31) 1.238(4), Zn(1)-N(1) 2.181(3), Zn(1)-N(2) 2.159(3) Å; O(1)-Zn(1)-O(2) 86.99(9), O(1)-Zn(1)-O(4) 91.01(9), O(1)-Zn(1)-O(7) 87.40(9), O(1)-Zn(1)-N(2) 179.16(9), O(1)-Zn(1)-N(1) 96.02(9), O(2)-Zn(1)-O(4) 85.76(9), O(2)-Zn(1)-O(7) 173.14(8), O(2)-Zn(1)-N(1) 90.72(9), O(2)-Zn(1)-N(2) 93.60(9), O(4)-Zn(1)-O(7) 90.40(9), O(4)-Zn(1)-N(1) 171.98(9), O(4)-Zn(1)-N(2) 88.43(10), O(7)-Zn(1)-N(1) 93.79(9), O(7)-Zn(1)-N(2) 91.98(10), N(1)-Zn(1)-N(2) 84.59(10) °; ; H(2)-O(3) 1.72(5), ∠O(1)-H(2)...O(3) 169(4) °.

Materials Chemistry

TGA data for $RZnO_2CR_f$ complexes (**1**, **3**, **5**, **7**) are shown in Fig. 8 and reveal quite different behaviour for the species with $R_f = C_3F_7$ (**3,7**) to those with the shorter C_2F_5 function (**1**, **5**).

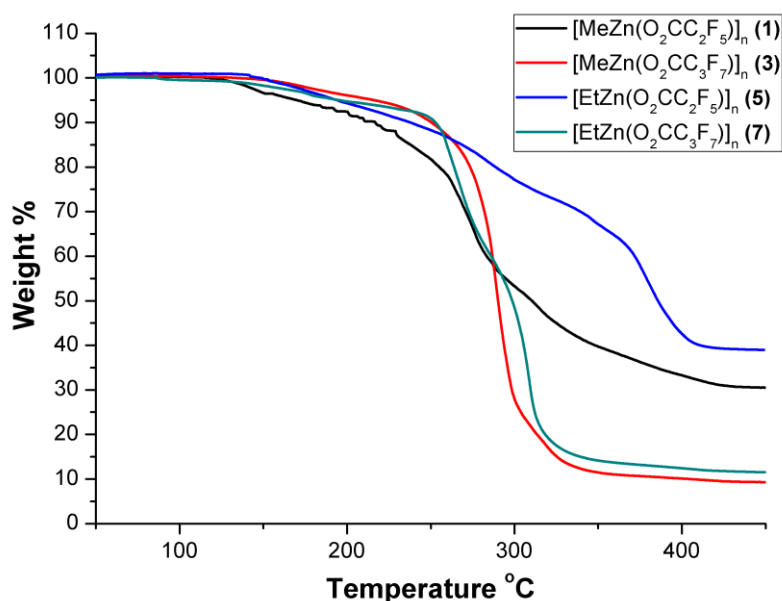


Figure 8. TGA data for $RZnO_2CR_f$ (**1**, **3**, **5**, **7**)

All four species show an initial weight loss of ca 5% (R = Me) or 10% (R = Et), starting at ca. 130°C, which are consistent with the loss of R (presumably as R-R or RH). Thereafter, both **1** and **5** undergo an ill-

defined series of decomposition steps ultimately leaving a residue at ca. 430 °C of 30.5 and 38.9 %, respectively; these values correspond most closely to either ZnO (33.0 %) or ZnF₂ (39.9 %) for **1**, **5**. The formation of ZnF₂ is plausible given the close intermolecular Zn...F contact seen in the solid-state structure (ESI), analogous to that seen in **7** (Fig. 1), and the precedent for the formation of metal fluorides from, for example, metal fluoroalkoxides, under similar circumstances.³⁵ When a larger sample of **5** was heated to 400°C under N₂, the temperature maintained for 1 hour and then cooled to room temperature at 1°C/min, the black residue (11.6 % carbon impurity) that remained was shown to be tetragonal ZnF₂ by PXRD (Fig. 9). While accurate quantitative EDX analysis proved difficult due to sample charging, the atomic ratios broadly correspond to a mixture of largely ZnF₂ with a second, oxygen-containing species which is possibly Zn(OH)F but there is no direct evidence for this in the PXRD (Fig. 9) (EXD atomic % found: Zn 28.9, F 60.2, O 5.5; calc. for 0.18 Zn(OH)F + 0.82 ZnF₂ = Zn 31.4, F 57.2, O 5.7). Annealing in air converted the sample to a white crystalline material which EDX suggests contains only traces of fluorine (ca. 3.2±1.7 atom%) and whose PXRD pattern can be indexed to ZnO (ESI), with quantitative EDX approximating to ZnO_{1.17} with negligible carbon contamination (< 0.1 %).

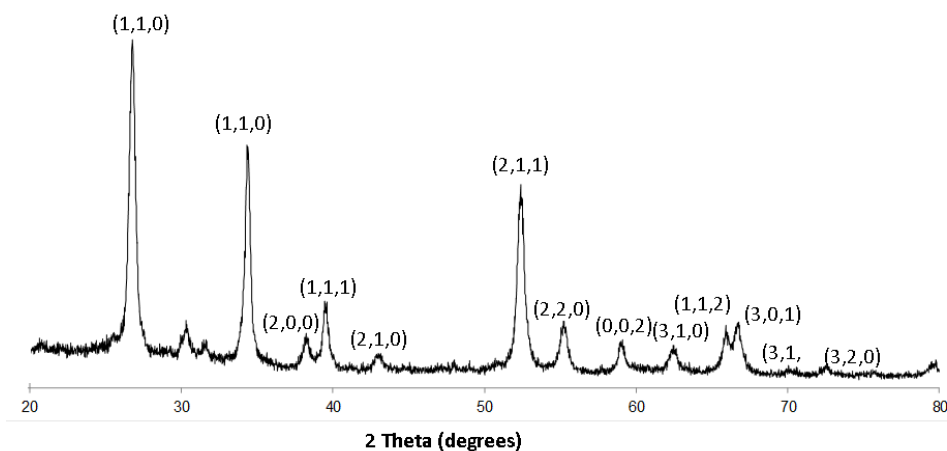


Figure 9 PXRD of the sample obtained by thermolysis of **5** under N₂ at 400 °C. The pattern is indexed to tetragonal ZnF₂ (PDF 89-5014).

Compounds **3** and **7** undergo more clearly defined decomposition steps at $T > \text{ca. } 250\text{ }^{\circ}\text{C}$ though we cannot make any rationale assignments to these processes. The residues (9.3, 11.5 % for **3**, **5**, respectively) are well below the values for either ZnO or ZnF₂ and strongly imply that these compounds are volatile.

3 was chosen as the precursor for CVD trials due to its superior volatility; LPCVD (47.2 Torr) was the chosen technique as the precursor was not deemed volatile enough for APCVD. Films were grown at 450°C onto glass over a period of 2 hours with the line and bubbler temperatures set to 150°C. Films were transparent and did not conduct to any notable extent when tested with a voltammeter. SEM imaging (Fig. 10a) reveals a uniform film consisting of crystallites of ca. 50 – 100 nm with cracks between clusters of these crystallites; EDX confirms the presence of Zn and O but could not detect any F in the film. PXRD confirms that a highly oriented ZnO film has been produced with a very intense peak corresponding to the (002) reflection (Fig. 10b). The morphology of the ZnO crystallites does merit further comment. The common modification of ZnO thin films is usually as hexagonal rods, in which polar (001) faces are parallel to the substrate i.e the *c*-axis and the substrate are parallel. In such a circumstance, the polar faces, which are commonly believed to be the active sites in various catalytic processes, are (i) in low abundance compared to the non-polar walls of the hexagon and (ii) largely inaccessible.^{36,37} The growth of vertically-aligned hexagonal microplates, in which the (001) face (*c*-axis) is perpendicular to the substrate, have larger surface area of available polar faces, and are seen to be more reactive e.g. enhanced photocatalytic activity.³⁸ The enhanced intensity of the (002) reflection, such as seen in Fig. 10b, can arise from preferred (001) growth (e.g. the vertically-aligned hexagon modification with the *c*-axis perpendicular to the substrate) or from a larger number of (001) faces (the common hexagonal rod morphology but with the *c*-axis parallel to the substrate). Although the SEM image of the films deposited from **3** are of low-resolution (Fig. 10a), they appear to show clusters of vertically-aligned plates which combine into pseudo-spherical aggregates; they are certainly not consistent with the more common hexagonal rod morphology.

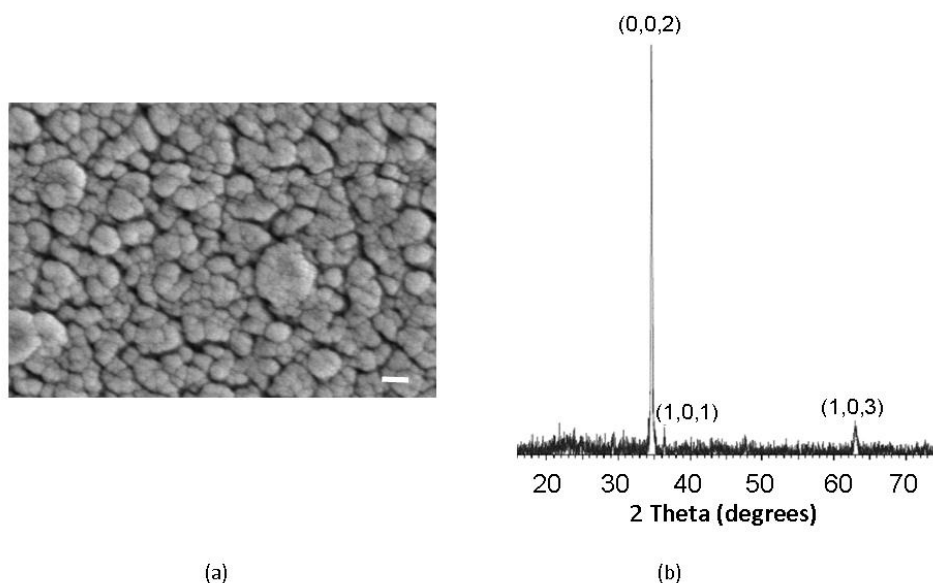


Figure 10. (a) SEM of the film grown from **3** by LPCVD, (b) PXRD of the film; indexing is to ZnO (PDF 89-1397); bar = 100 nm.

Clearly, in the gas phase any weak intermolecular Zn...F interactions (such as in **5** or **7**) will have little, if any, influence on the film deposited, and the lack of halogen in the final film suggests that decomposition eliminates the fluorocarbon groups, as, for example, $(R_f)_2CO$ or $[(R_f)_2CO]_2O$ by analogy with the decomposition of $Zn(O_2CCH_3)_2$.³⁹

TGA data for the TMEDA adducts $RZnO_2CR_f.TMEDA$ (**9** - **12**) (Fig. 11) show relatively consistent behaviour with no distinction between compounds with different R_f groups. Data for **11** show a three stage process, starting with loss of the ethyl group (observed residual mass 87.4, theoretical 92.2 %), then loss of TMEDA (observed residual mass 61.3, theoretical 61.0 %), and finally decomposition of the carboxylate group leaving a residual mass of 21.4% compared to 21.5 % expected for ZnO. It is likely that the remaining compounds **9**, **10**, **12** follow a similar pattern, though the above steps are not as clearly differentiated as for **11**. Films grown using **10** as precursor by LPCVD (39.6 Torr) on glass substrates at a reactor temperature of 400°C, with a line and bubbler temperature of 90 °C over a duration of 90 mins. lead to granular (100-150 nm in diameter) ZnO films oriented in the (002) direction (ESI), very similar to those deposited from **3** Fig. 10); EDX showed no evidence for fluorine incorporation into the film, nor were the films conducting.

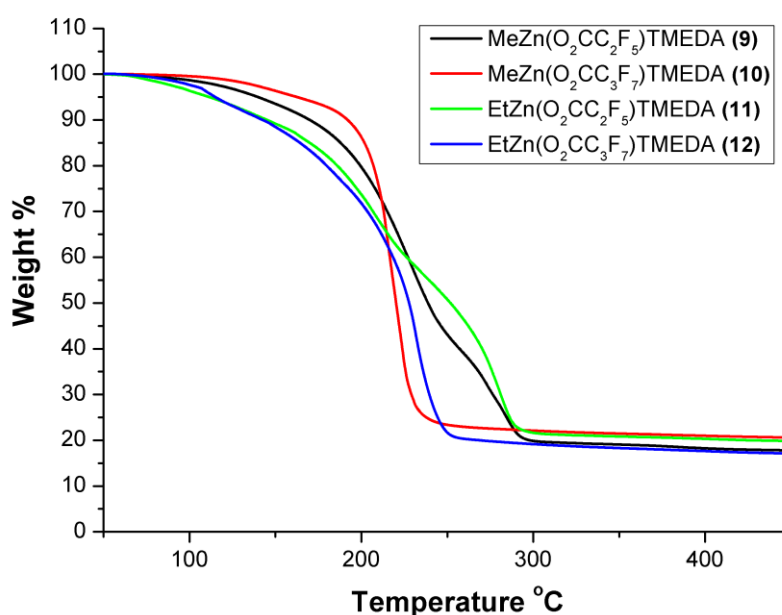


Figure 11. TGA data for $RZnO_2CR_f.TMEDA$ (**9** - **12**)

The purely inorganic precursors $\text{Zn}(\text{O}_2\text{CR}_i)_2\cdot\text{TMEDA}$ (**13**, **14**) decompose in essentially a single concerted step (Fig. 12), though a second stage in the decomposition of **14** at $T > 290^\circ\text{C}$ is visible. In both cases the remaining residue at 350°C (6.25, 12.3 % for **13**, **14**, respectively) is less than that expected for ZnO (15.8, 13.2 %, for **13**, **14**, respectively), indicating some volatility to these species.

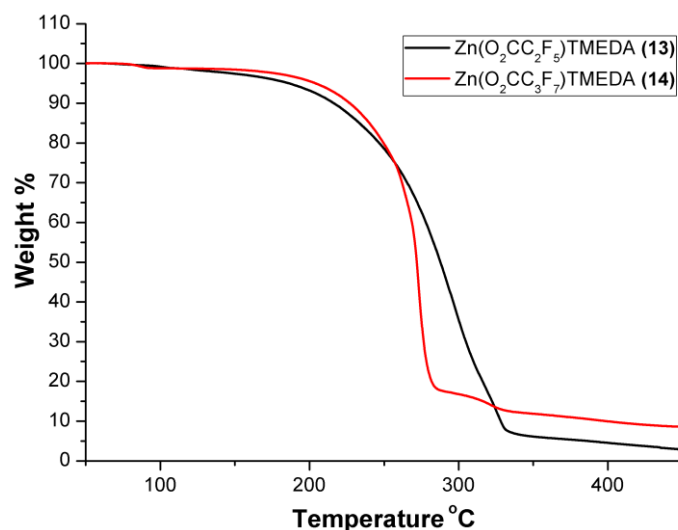


Figure 12. TGA data for $\text{Zn}(\text{O}_2\text{CR}_i)_2\cdot\text{TMEDA}$ (**13**, **14**)

LPCVD using **13** as precursor (glass substrate, reactor temperature 450°C , bubbler and line temperatures 150°C , 120 min., 39.8 Torr) yielded a textured, fluorine-free ZnO film comprising very small spheres (ca. 20 nm in diameter), cracked around clusters of varying size of these spheres. PXRD confirms the films are ZnO but lack the preferred orientation shown in the films grown from **3** or **10** (Fig. 13)

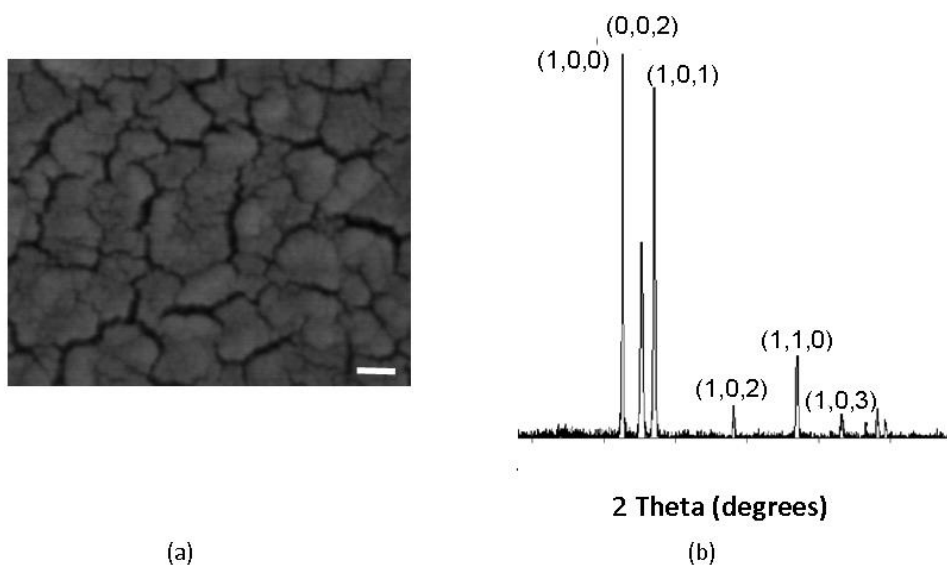


Figure 13. (a) SEM of the film grown from **13** by LPCVD, (b) PXRD of the film; indexing is to ZnO (PDF 89-1397).

Conclusions

Zinc fluorocarboxylates, either RZnO_2CR_f , $\text{RZnO}_2\text{CR}_f\cdot\text{TMEDA}$ or $\text{Zn}(\text{O}_2\text{CR}_f)_2\cdot\text{TMEDA}$, can be used to deposit ZnO by LPCVD at 400 °C by do not result in measurable fluorine incorporation into the films. Conversely, $\text{RZnO}_2\text{C}_2\text{F}_5$, which shows close intermolecular Zn...F contacts in the solid state, decomposes in the bulk to ZnF_2 . The only other report we can find concerning the synthesis of a single-source precursor for the deposition of ZnO:F relates to $\text{EtZn}[\text{OC}(\text{Me})(\text{CF}_3)_2]$, but no materials chemistry was reported.⁴⁰ However, similar tin $[\text{Sn}(\text{OCH}(\text{CF}_3)_2)_4(\text{HNMe}_2)_2]$ ⁴¹ and indium alkoxides $[\text{In}(\text{OCMe}(\text{CF}_3)_2)_3(\text{H}_2\text{NBu}^\dagger)]$ ⁴² do deposit fluorine-doped SnO_2 or In_2O_3 , respectively. Interestingly, the incorporation of fluorine into In_2O_3 from the fluoroalkoxide does not occur at 550 °C, in contrast to 2-3 atom% at $T < 500$ °C,⁴² and in the case of ZnO:F (prepared by spray pyrolysis) the composition changes from $\text{ZnO}_{0.90}\text{F}_{0.10}$ at 400 °C to $\text{ZnO}_{0.94}\text{F}_{0.06}$ at 525 °C i.e. loss of dopant is relatively facile and thus temperature sensitive.⁴³ Moreover, in the structure of $[\text{In}(\text{OCH}(\text{CF}_3)_2)_4(\text{H}_2\text{NBu}^\dagger)][\text{H}_3\text{NBu}^\dagger]^+$ there is a close intramolecular In...F contact (2.924 Å),⁴⁴ well with the sum of the van der Waals radii (3.45 Å) despite the fact that it incorporates five-coordinate indium. An even shorter In...F contact is present in $[\text{In}(\text{OCMe}(\text{CF}_3)_2)_3]_2$ (2.809 Å) which contains a four-coordinate metal,⁴⁴ and these, along with their intramolecular nature, may account for the success in the indium system which is lacking with our zinc compounds.

Acknowledgements

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Supporting Information

Crystallographic data for the structural analysis (in CIF format) have been deposited with the Cambridge Crystallographic Data Center, CCDC nos. 910799 – 910806 for **2**, **5 - 8**, **11**, **13**, **15**, respectively. Copies of this information may be obtained from the Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (Fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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Graphical Abstract

The organozinc fluoro-carboxylates $RZnO_2CR_f$, $RZnO_2CR_f \cdot TMEDA$ and $Zn(O_2CR_f)_2 \cdot TMEDA$ ($R = Me, Et$; $R_f = C_2F_5, C_3F_7$) have been synthesised and representative examples structurally characterised. While $EtZnO_2CC_2F_5$ decomposes in the bulk to ZnF_2 , under LPCVD conditions $MeZnO_2CC_3F_7$ and $MeZnO_2CC_3F_7 \cdot TMEDA$ give highly-oriented, but fluorine-free, ZnO.

